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Scaling and Optimization of Ferroelectric Hafnium Oxide for Memory Applications and Beyond

Johannes Müller, Patrick Polakowski and Stefan Riedel

[1] Fraunhofer IPMS-CNT
Dresden, Germany
E-mail: johannes.mueller@ieee.org

Abstract

Ferroelectric hafnium oxide based systems have emerged as a new class of CMOS-compatible, scalable, 3D-capable and lead-free ferroelectrics striving to renew the scaling potential of ferroelectric memories. However, considering the multitude of unique physical characteristics provided by ferroelectrics and the industrial acceptance of HfO_2 and ZrO_2 based systems a much broader application space can be envisioned. Especially ferroelectric HfO_2-ZrO_2 thin films and its laminates with Al_2O_3 provide the flexibility and manufacturability required for an application specific tailoring of material properties.

1. Introduction

Ferroelectrics are best described by a spontaneous polarization switchable in an external electric field. In order for this phenomenon to be observable the coercive field strength of the material has to be significantly below the dielectric breakdown field. It is interesting to note that this unique feature so far only knows one application - ferroelectric memories. Nevertheless, over the last decades this single application has clearly become the major driving force for making ferroelectrics durable, scalable and available to CMOS technology. However, the much broader application space ferroelectrics are best known for is provided by their subgroup relationship to pyroelectrics, piezoelectrics and ultimately dielectrics. Here, although mostly restricted to discrete components, the usage of ferroelectric or antiferroelectric thin films spans from ultrasonic transducers and micro actuators to pyroelectric infrared sensors and high energy storage capacitors. However, the progressive miniaturization in those fields as well as the increasing demand for more and more functionality per chip yields new potential for ferroelectrics integrable with CMOS. Especially new tasks such as sensing and energy harvesting clearly reach beyond the pioneering memory applications.

With ferroelectric hafnium oxide (FE-HfO_2) a CMOS-compatible, scalable, 3D-capable and lead-free material emerges that appears ideally suited for this new application space [1]. Primarily motivated by memory applications, thickness scaling to the single digit nanometer range [2], 3D-capacitor integration [3], as well as ferroelectric field effect transistor implementation at the 28 nm node [4] has already been demonstrated (Fig. 1). First results on non-memory applications of FE-HfO_2 such as negative capacitance FETs [5] or high energy storage capacitors using antiferroelectric hafnium oxide (AFE-HfO_2) [6] have already been reported. However, emerging applications such as piezoelectric or pyroelectric energy harvesters, pyroelectric infrared sensors or the feasibility of a FE-HfO_2 based ferroelectric tunnel junction (FTJ) have yet to be demonstrated.

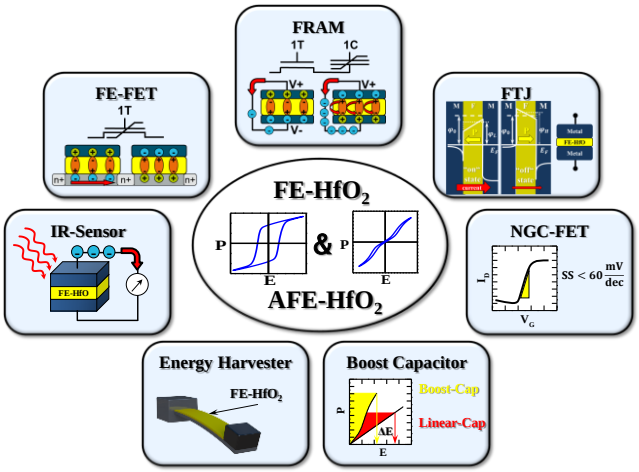

Fig. 1 System on Chip application potential of a CMOS-compatible ferroelectric

In order to provide functionality for this broad application range, as well as flexibility within each application, the ferroelectric characteristics of the material should be independent of important design or manufacturing parameters such as film thickness, topography, process variations or thermal budget. In this contribution we will show that ferroelectric HfO_2-ZrO_2 (HZO) and its laminates with Al_2O_3 are ideally suited for an application specific tailoring of material properties. Due to the limited extend, only the thickness scalability as well as the 3D-capability of this material system are covered within this abstract.

2. Experimental

The HZO films were deposited by atomic layer deposition (ALD) using a single wafer warm wall reaction chamber. Tetrakis(ethylmethylamino)hafnium (TEMAHf) and Tetrakis(ethylmethylamino)zirconium (TEMAZr) were used as precursors to deposit the mixed HZO films, while ozone was used as co-reactant. The HZO films were deposited by alternating TEMAHf and TEMAZr based processes with a cycle ratio of 1:1 resulting in a Hf/Zr cation ratio of ~50% indicating a similar growth per cycle of the individual precursors. As deposited films were x-ray amorphous and subjected to crystallization anneals to form the ferroelectric orthorhombic phase. Laminated films were deposited by intercepting the HZO deposition every 5 nanometer with

0.5 nm Al_2O_3. Al_2O_3 was deposited using Trimethylaluminium (TMA), which was supplied by bubbling at room temperature, and ozone. Titanium nitride was used as top and bottom electrode to form MIM capacitors.

3. Results and Discussion

Compared to the doped FE-HfO_2 systems [7], which react quite sensitive to small stoichiometry variations, ferroelectricity in the HfO_2-ZrO_2 solid solution is rather easily achieved [8]. In this system ferroelectric phase stability spans a broad compositional range, providing a clear advantage in terms of process stability and variability. However, as a result of the rather low crystallization temperature of HfO_2-ZrO_2, which decreases even further with increasing thickness, premature crystallization during deposition and extensive grain growth and grain boundary extension during thermal treatments may occur. This leads to a degradation of reliability properties and ferroelectric characteristics. A quite similar reliability problem was encountered when ZrO_2 was first suggested as a node dielectric for advanced DRAM manufacturing. To circumvent these issues with pure ZrO_2, Al_2O_3 separated laminates were introduced that came to be known as ZAZ [9]. Following up on this approach, the insertion of Al_2O_3 interlayers was applied to ferroelectric HfO_2-ZrO_2 in a similar manner. The polarization-voltage (P-V) results for a 5 nm, 10 nm (one Al_2O_3 interlayer) and a 15 nm (two Al_2O_3 interlayers) thick HfO_2-ZrO_2 thin film are depicted in Fig. 2. In agreement with [10] it is clearly observed that the ferroelectric properties remain stable despite the insertion of one Al_2O_3 layer. Here, the sample with two Al_2O_3 insertions shows that this concept can be extended even further. The limits and boundary conditions of this concept will be elaborated within the full version of this contribution.

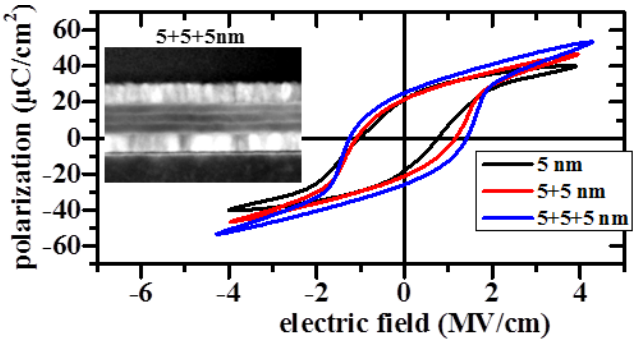

Fig. 2 P-V characteristics of 5, 10 and 15 nm HfO_2-ZrO_2 thin films stacked with no, one and two Al_2O_3 interlayers, respectively. Inset is showing a STEM micrograph of the triple stack.

Yet another key to the enduring success of ZAZ in DRAM manufacturing is provided by its excellent step coverage in high aspect ratio structures, enabling 3D stack or trench capacitor integration. Primarily for future nodes of ferroelectric random access memory, but also for other densely packed applications, the availability of a 3D-capable ferroelectric is of similarly high interest. Figure 3 shows first results of a 3D-integrated, ferroelectric HZO thin film laminated with Al_2O_3. The TEM micrographs depicted in Fig. 3a clearly show that excellent step coverage can be achieved and that the laminated structure is preserved down to the very bottom of the 1.6 µm deep trenches. The P-V characteristics plotted for different trench counts in Fig. 3b provide electrical evidence for a stable ferroelectric phase along the entire sidewall of the trenches. A detailed investigation of the 3D-integrated and laminated HZO capacitors will be given in the full contribution.

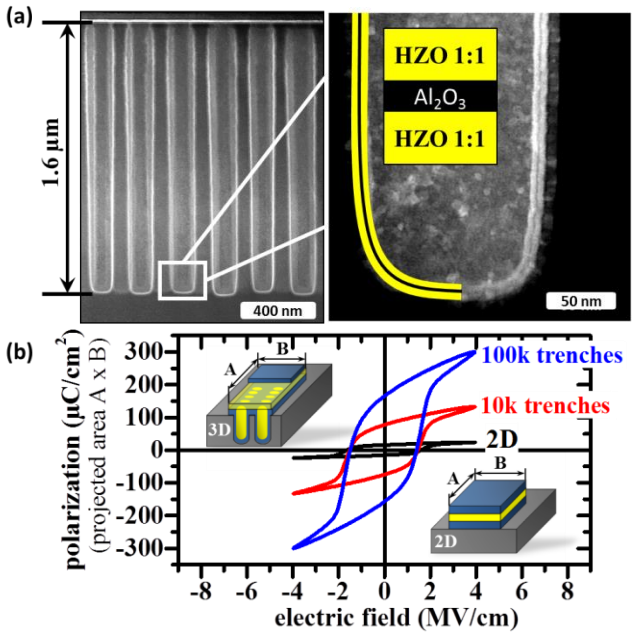

Fig. 3 (a) TEM micrographs of Al_2O_3 laminated HZO thin films integrated into deep trench capacitors. (b) Corresponding P-V characteristics for different trench counts.

4. Conclusions

FE-HfO_2 provides the possibility to directly implement ferroelectric, pyroelectric or piezoelectric devices into standard CMOS technologies and therewith opens up a new pathway to advanced system on chip functionalization. The easy stoichiometry control, the excellent 3D-capability as well as the thickness independent ferroelectric characteristics of Al_2O_3 laminated HfO_2-ZrO_2 renders it the ideal material to cope with a wide range of different applications.

Acknowledgements

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